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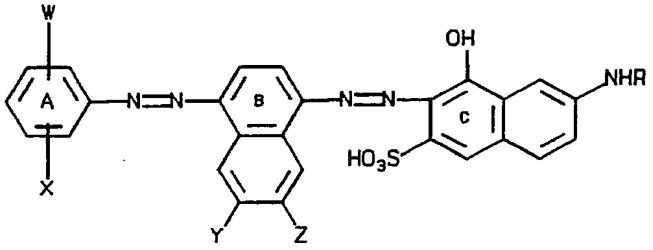
(54) Ink

(57) An ink suitable for use in ink jet printing comprising a solution of a colorant in an aqueous medium, the colorant comprising at least 80% by weight of a water-soluble black dye of Formula (1)



(1)

wherein

W is COOH

X is H, COOH, SO^3H, halo, hydroxy, nitro, cyano, C_{1-6}-alkyl, C_{1-6}-alkoxy, or C_{1-6}-acylamino;

Y is H, COOH or SO_3H;

Z is H, COOH or SO_3H; and

R is H or C_{1-4}-alkyl;

provided that there are at least two COOH groups and that the number of COOH groups is equal to or greater than the number of SO_3H groups and up to 20% of one or both of two other water-soluble dyes, one of which is a defined yellow dye and the other is a defined cyan dye.

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INK

This specification describes an invention relating to an ink suitable for use in ink jet printing and, in particular, a neutral black ink with good wet-fastness.

According to the present invention there is provided an ink comprising a solution of a colorant in an aqueous medium, the colorant comprising at least 80% by weight of a water-soluble black dye of Formula (1) as hereinafter defined and up to 20% of one or both of two other water-soluble dyes, one of which is a yellow dye of the Formula (2) as hereinafter defined and the other is a cyan dye of Formula (9) as hereinafter defined.

The colorant preferably comprises at least 85%, more preferably at least 90% and preferably up to 98% by weight of the black dye and up to 15% by weight of the yellow and/or the cyan dye, more preferably up to 10% and preferably at least 2%. One specifically preferred colorant comprises from 90% to 95% of the black dye and from 10% to 5% of the cyan dye, another specifically preferred colorant comprises from 90% to 98% of the black dye and from 10% to 2% of the yellow dye and another specifically preferred colorant comprises from 90% to 98% of the black dye and from 10% to 2% of a mixture of the yellow dye and the cyan dye. The mixture of yellow and cyan dyes preferably comprises from 90:10 to 10:90, more preferably from 80:20 to 20:80 and especially from 60:40 to 40:60 by weight of yellow dye to cyan dye.

The amount of the colorant in the ink is preferably from 0.5% to 20%, more preferably from 0.5% to 15% and especially from 1% to 5%, by weight with respect to the total weight of the ink. The aqueous medium is preferably substantially water but preferably comprises up to 20%, more preferably up to 15% and especially up to 10%, by weight of one or more water-soluble organic liquids. The ink may also comprise other conventional additives, especially those used in ink jet printing inks.

The water-soluble organic liquid(s) is conveniently selected from C_{1-4}-alkanols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol and isobutanol; amides such as dimethylformamide and dimethylacetamide; ketones and ketone alcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; alkylene glycols or thioglycols containing a C_2-C_6 alkylene group such as ethylene glycol, propylene glycol, butylene

glycol, pentylene glycol and hexylene glycol,; poly(alkylene-glycol)s and thioglycol)s such as diethylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols such as glycerol and 1,2,6-hexanetriol; and lower alkyl glycol and polyglycol ethers, such as 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)-ethoxy] ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol; or a mixture containing two or more of the aforementioned water-soluble organic liquids.

However it is preferred that the organic liquid(s) is selected from heterocyclic ketones or sulphones, such as 2-pyrrolidone, N-methyl-2-pyrrolidone, N-(2-hydroxyethyl)-2-pyrrolidone and sulpholane, especially 2-pyrrolidone and sulpholane. Other preferred organic liquids are 2-(2-butoxyethoxy)ethanol and n-pentan-1,4-diol.

We have found that the present inks, wherein the medium contains up to 20% by weight of one or more of these preferred organic liquids, especially 2-pyrrolidone, are more stable than equivalent inks wherein the medium contains one or more of the other aforementioned organic liquids.

Examples of other ingredients which may be present in the inks are a penetrant, to assist permeation of the dye into a paper substrate, a kogation-reducing agent, to prevent or reduce the build-up of residue (koga) on the resistor surface in thermal ink jet printers, and a buffer, such as sodium borate, to stabilise the pH of the ink.

The kogation-reducing agent is preferably an oxo anion, such as described in EP 425150A. The oxo-anion may be $C_2O_4^{2-}$, SO_3^{2-}, SO_4^{2-}, molybdate, AsO_4^{3-} or more preferably a phosphate ester, a diorgano-phosphate or more especially a phosphate salt which is particularly effective in reducing kogation. Examples of phosphate salts are dibasic phosphate (HPO_4^{2-}), monobasic phosphates ($H_2PO_4^-$) and polyphosphates ($P_2O_7^{4-}$). The selection of the counterion is not believed to be critical and examples include alkali metals, ammonium and alkylammonium cations. The amount of kogation-reducing agent in the ink is preferably from 0.001% to 15%, based on oxo-anion, and more preferably from 0.01% to 1%, by weight with respect to the total ink.

A further aspect of the present invention provides a process for printing a substrate with an ink as hereinbefore defined by ink jet printing.

In ink jet printing an ink is formed into small droplets by ejection from a reservoir through a small orifice so that the droplets of ink are directed at a substrate. Suitable ink jet printing processes for the present ink are piezoelectric ink jet printing, and more especially thermal ink jet printing. In thermal ink jet printing, programmed pulses of heat are applied to the ink by means of a resistor, adjacent to the orifice during relative movement between the substrate and the reservoir.

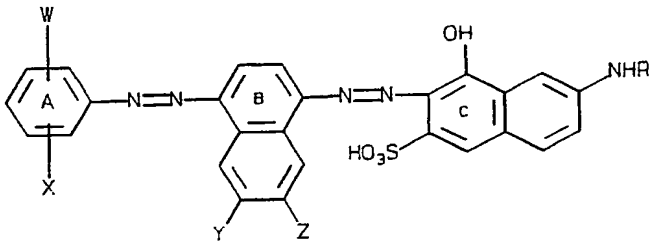
Preferred substrates include cellulosic sheet materials, such as clear cellulosic sheets suitable for projector slides and more preferably paper, especially plain paper, which may be acidic, alkaline or neutral.

According to a further aspect of the present invention there is provided a cellulosic substrate, especially paper or a projector slide printed with an ink according to the invention.

Although the ink may contain other dyes than those hereinbefore defined, it preferably free from such other dyes as the ink containing only the hereinbefore defined dyes in the preferred proportions has a particularly attractive neutral black shade and especially high wet-fastness on cellulosic substrates.

Black Dye

The black dye, in the free acid form, has the Formula (1):



(1)

wherein

W is COOH

X is H, COOH, SO^3H, halo, hydroxy, nitro, cyano, C_{1-6}-alkyl, C_{1-6}-alkoxy, or C_{1-6}-acylamino;

Y is H, COOH or SO_3H;

Z is H, COOH or SO_3H; and

R is H or C_{1-4}-alkyl;

provided that there are at least two COOH groups and that the number of COOH groups is equal to or greater than the number of SO_3H groups.

The group X is preferably selected from H; COOH; SO_3H; halo especially chloro or bromo; hydroxy; nitro; cyano; C_{1-4}-alkyl especially methyl; C_{1-4}-alkoxy especially methoxy; and C_{1-4}-alkylcarbonylamino; especially acetamido. However X is more preferably H or COOH, and especially COOH.

Where X is H, the COOH group on Ring A represented by W may be in the ortho, meta or para position with respect to the azo group but is preferably in the meta or para position. However, it is preferred that X is COOH and that the two COOH groups are in the 3,4-, 2,5- and especially the 3,5- positions on Ring A.

The black dye preferably contains from 2 to 4 COOH groups and preferably not more than two SO_3H groups, i.e. not more than one of X, Y and Z is SO_3H, i.e. there are preferably the same number of COOH and SO_3H groups or an excess of 1 or 2 COOH groups.

The group R is preferably H or methyl, and more especially H.

Preferred diazo components from which Ring A is derivable are, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, 2-aminophthalic acid, 3-aminophthalic acid, 4-aminoisophthalic acid, 2-aminoisophthalic acid, 2-aminoterephthalic acid and especially 5-aminoisophthalic acid,

Preferred couplers from which the central group B is derivable are, 1,6-Cleves acid, 1,7-Cleves acid, mixed Cleves acids, 8-amino-2-naphthoic acid, 5-amino-2-naphthoic acid and 5-amino-2,3-dicarboxynaphthalene and especially 1-naphthylamine.

Preferred couplers from which the third group C is derivable are, N-methyl-Gamma acid, N-butyl-Gamma acid and especially Gamma acid.

Suitable black dyes of Formula $(1)^-$, in the ammonium ($^+NH_4$) salt form, in which R is H are set out in the following table:

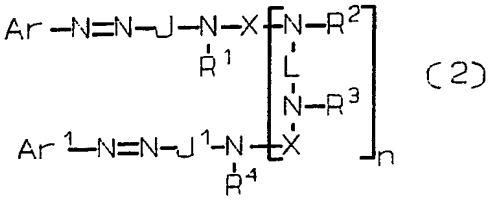
Dye	X	W	Y	Z;	Dye	X	W	Y	Z
B1	3-COOH	5-COOH	H	H;	B8	3-COOH	5-COOH	COOH	H;
B2	3-COOH	5-COOH	H	SO_3H;	B9	3-COOH	5-COOH	H	COOH;
B3	3-COOH	5-COOH	SO_3H	H;	B10	3-COOH	5-COOH	COOH	COOH;
B4	H	4-COOH	H	COOH;	B11	H	3-COOH	COOH	H;
B5	H	3-COOH	H	COOH;					
B6	2-COOH	5-COOH	H	H;	B12	2-COOH	3-COOH	H	H;
B7	2-COOH	4-COOH	H	SO_3H;	B13	3-COOH	4-COOH	H	H;

Preferred black dyes are Dye B2 and, more especially, Dye B1.

The black dye is described in greater detail in EP 356,080 the contents of which are incorporated herein by reference.

Yellow Dye

The yellow dye, in the free acid form, has the structure shown in Formula (2):



(2)

wherein:

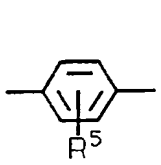
Ar and Ar^1 are each independently aryl or substituted aryl providing at least one of Ar and Ar^1 has at least one substituent selected from COOH and COSH;

R^1, R^2, R^3, and R^4 are each independently H, alkyl or substituted alkyl;

L is a divalent organic linking group;

n is 0 or 1;

J and J^1 are each independently of formula (3), (4) or (5):



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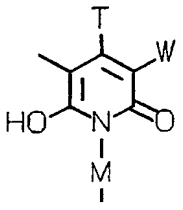

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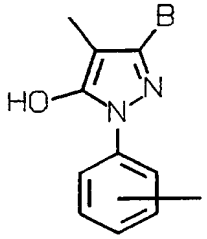


(5)

wherein

each R^5 is independently selected from H, alkyl, substituted alkyl, alkoxy, halogen, CN, ureido and $NHCOR^6$;

R^6 is H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl;

each T is independently alkyl;

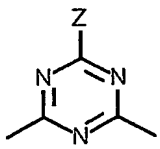
each W is independently selected from H, CN, $CONR^{10}R^{11}$, pyridinium and COOH;

each M is an alkylene chain having 2 to 8 carbon atoms;

B is H, alkyl or COOH; and

R^{10} and R^{11} are each independently H, alkyl or substituted alkyl;

each X is independently carbonyl or a group of the Formula (6), (7) or (8):



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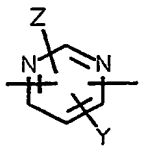

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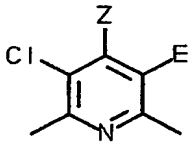


(8)

wherein

Z is OR^7, SR^7 or NR^8R^9;

Y is H, Cl, CN or Z;

E is Cl or CN; and

R^7, R^8 and R^9 are each independently H, alkenyl, substituted alkenyl, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl, or

R^8 and R^9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring;

provided that

(a) if the compound of Formula (2) has no $-SO_3H$ groups then it has at least two groups selected from -COOH and -COSH;

(b) the compound of Formula (2) has at least as many groups selected from -COOH and -COSH as $-SO_3H$ groups; and

(c) that the structures of the groups Ar-N=N-J and Ar-N=N-J^1 are such that the compound of Formula (2) is yellow.

It is preferred that the yellow dye of Formula (2) has at least as many -COOH as $-SO_3H$ groups and, if it has no $-SO_3H$ groups that it has at least two and, more preferably at least three, -COOH groups. It is especially preferred that the yellow dye has up to 2 $-SO_3H$ groups and from 2 to 5 -COOH. It is also preferred that the yellow dye is free from cellulose reactive groups.

The groups Ar and Ar^1 are preferably independently selected from phenyl and substituted phenyl. Each optional substituent on Ar and Ar^1 is preferably selected from optionally substituted alkyl, especially C_{1-4}-alkyl; alkoxy, especially C_{1-4}-alkoxy; $-SO_3H$; $-PO_3H_2$; -COSH; -OH; $-CO_2H$; and halogen, especially Cl or Br. It is especially preferred

that when Ar or Ar^1 is substituted phenyl, each substituent is independently selected from CO_2H, COSH and SO_3H, and more especially each substitutent is CO_2H. In especially preferred structures, at least one of Ar and Ar^1 has at least one -COOH and it is further preferred that each of Ar and Ar^1 has at least one -COOH and more preferably at least two -COOH groups, for example, dicarboxyphenyl. It is preferred that both Ar and Ar^1 are the same, and more especially that each is 3,5-dicarboxyphenyl.

It is preferred that each of J & J^1 is of Formula (3) and that each R^5 is independently selected from H, optionally susbtituted C_{1-4}-alkyl, C_{1-4}-alkoxy, Cl, CN, Br, ureido and $NHCOR^6$, more preferably H, C_{1-4}-alkyl, C_{1-4}-alkoxy, ureido and $NHCO(C_{1-4}$-alkyl), and especially H, methyl, methoxy or ureido. When R^5 is not H it is preferably ortho with respect to the azo group (-N=N-).

When J and J^1 are of Formula (4) or (5), each T is preferably independently C_{1-6}-alkyl, especially C_{1-4}-alkyl; the group M may be branched chain alkylene but is preferably straight chain alkylene; W is preferably H, CN, $CONR^{10}R^{11}$ or COOH; R^6 is preferably H, C_{1-4}-alkyl, phenyl or $(CH_2)_{1-4}$-phenyl, each of which may be unsubstituted or substituted, and more especially C_{1-4}-alkyl and B is preferably H.

It is preferred that n is 0 so that the two amino groups, NR^1 and NR^4, are linked by a single group, X, and it is further preferred that X is of Formula (6).

Z is preferably NR^8R^9, especially NHC_2H_4OH, $N(C_2H_4OH)_2$, morpholino, $NH(C_{1-6}$-alkyl), $NH-(CH_2)_2-CO_2H$, $NHCH_2C_6H_4CO_2H$, mono- or di-carboxyanilino, $NHC_6H_4SO_3H$ or $NHCH_2SO_3H$.

R^1, R^2, R^3 and R^4 are preferably each independently H, C_{1-4}-alkyl or C_{1-4}-hydroxyalkyl, and more especially H.

R^7, R^8 and R^9 are preferably independently selected from H, optionally substituted C_{1-6}-alkyl, C_{3-4}-alkenyl, optionally substituted phenyl and optionally substituted $(CH_2)_{1-4}$-phenyl, more preferably from H, allyl, C_{1-4}-alkyl, benzyl, C_{1-4}-hydroxyalkyl and especially from H, methyl, ethyl and 2-hydroxyethyl. The optional substituents on R^7, R^8 and R^9 are preferably independently selected from -OH, $-SO_3H$ and -COOH, especially -OH. When R^8 and R^9 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring this is preferably a morpholine or piperidine ring.

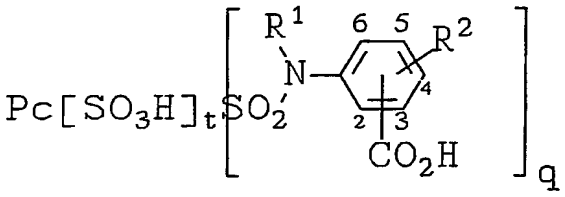
The yellow dye is described in greater detail in EP 468,647 the contents of which are incorporated herein by reference.

An especially preferred yellow dye, hereinafter called Dye Y1, is a dye of Formula (2) in which Ar and Ar^1 are both 3,5-dicarboxy-phenyl; J and J^1 are both phen-1,4-ylene; R^1 and R^4 are both H; n is 0; X is of Formula (6) and Z is morpholino, in the ammonium ($^+NH_4$) salt form.

Cyan Dye

The cyan dye, in the free acid form, has the structure shown in Formula (9) or the structure shown in Formula (10).

(a) Cyan dye of Formula (9)



Formula (9)

wherein:

Pc is a metal-free or metal-containing phthalocyanine radical having a valency from 3 to 4;

R^1 is H, optionally alkyl, alkenyl or aralkyl;

R^2 is H, alkyl, alkoxy, halo or optionally substituted amino; and

(t+q) is from 3 to 4 inclusive.

In the dye of Formula (9), the COOH group is preferably at the 2-, 3-, 5- or 6-position, especially the 3-position, on the phenyl group.

The metal present in the metal-containing phthalocyanine radical may be any of the metals known to complex with phthalocyanine nuclei, but is preferably scandium, titanium, vanadium, chromium, manganese, iron, cobalt or zinc, more preferably nickel and especially copper. When the metal is tri- or tetra-valent, it may coordinate with chlorine or oxygen, e.g. VO, AlCl, $PbCl_2$.

The group R^1 is preferably H; C_{3-4}-alkenyl, such as allyl; optionally substituted C_{7-11}-aralkyl, especially benzyl; optionally substituted C_{1-4}-alkyl, especially methyl, ethyl or hydroxyethyl.

The group R^2 is preferably H; C_{1-4}-alkyl, especially methyl; C_{1-4}-alkoxy, especially methoxy; chloro; or an amino group, $-NX^1X^2$,

wherein X^1 and X^2 are each independently H, or optionally substituted alkyl or aryl. When X^1 or X^2 is alkyl it is preferably C_{1-18}-alkyl, more preferably C_{1-6}-alkyl. When X^1 or X^2 is optionally substituted aryl it is preferably optionally substituted phenyl, especially phenyl or phenyl having 1 or 2 substituents selected from C_{1-12}-alkyl, C_{1-12}-alkoxy, halo and carboxy. Examples of amino groups, NX^1X^2, are n-hexylamino, N,N-di-n-butylamino, phenylamino, methylamino, dimethylamino, diethylamino, dipropylamino, ethylamino, n-propylamino, n-butylamino, n-octylamino and 3-carboxyphenylamino.

It is especially preferred that R^1 and R^2 are both H.

The value of t is preferably at least 0.5, more preferably from 0.5 to 2, and especially about 1; the value of q is preferably greater than or equal to t, and especially about 3; and (t+q) is preferably 4. Where the value, of (t+q) is not integral, the dye of Formula (9) will actually comprise a mixture of dyes with different values of (t+q).

The cyan dye of Formula (9) is described in greater detail in EP 559309A the contents of which are incorporated herein by reference.

An especially preferred cyan dye, hereinafter called Dye C1, is of Formula (9) wherein Pc is copper phthalocyanine; R^1 and R^2 are both H, t is 1 and q is 3, and the COOH group is in the 3-position, in the ammonium ($^+NH_4$) salt form.

(b) Cyan dye of Formula (10)

$$Pc(SO_3H)_t(SO_2\text{-}NR^1\text{-}L\text{-}NR^2\text{-}X\text{-}NR^3\text{-}G)_q \qquad (10)$$

wherein:

Pc is a metal-containing phthalocyanine nucleus;

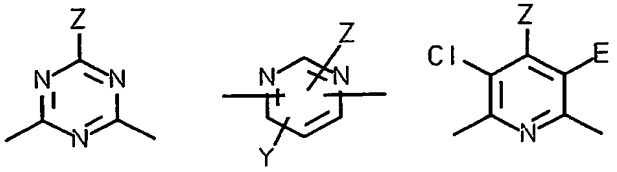
R^1, R^2 and R^3 are each independently H, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aralkyl or substituted aralkyl;

L is a divalent organic linking group;

G is a colourless organic radical substituted by one or two groups selected from COSH and COOH;

(t+q) is from 3 to 4 inclusive; and

each X independently is carbonyl or a group of formula (11), (12) or (13):



(11) (12) (13)

wherein:

each Z independently is NR^4R^5, SR^6 or OR^6;

each Y independently is H, Cl, Z, SR^7 or OR^7;

each E independently is Cl or CN;

R^4, R^5, R^6 and R^7 are each independently H, alkyl, substituted alkyl, aryl, substituted aryl, aralkyl or substituted aralkyl or R^4 and R^5 together with the nitrogen atom to which they are attached form a 5 or 6 membered ring.

The cyan dye of Formula (10) is preferably free from COSH groups and also preferably contains at least as many -COOH groups as $-SO_3H$ groups.

The metal present in the metal-containing phthalocyanine nucleus may be any of the metals known to be found in complex association with phthalocyanine nuclei, but is preferably selected from Sc, Ti, V, Cr, Mn, Fe, Co and Zn, and more especially from Ni and Cu. When the metal is tri- or tetra-valent, it may carry one or two chlorine atoms.

R^1, R^3, R^6 and R^7 are preferably each independently selected from H, C_{1-4}-alkyl and hydroxy-C_{1-4}-alkyl, more preferably H, and C_{1-4}-alkyl. It is particularly preferred that R^1 and R^3 are H.

The group R^2 is preferably H, C_{1-4}-alkyl, such as methyl or hydroxy-C_{1-4}-alkyl, such as hydroxyethyl.

The groups R^4 and R^5 are preferably each independently H, or optionally substituted C_{1-4}-alkyl, preferred substituents being -COOH, $-SO_3H$ or, more especially, -OH. Where R^4 and R^5 together with the N atom to which they are attached form a 5- or 6-membered ring, this is preferably morpholinyl or piperidinyl.

When X is of Formula (12), Z is preferably attached to the C atom between the two ring N atoms and Y is preferably para with respect to Z. However, X is preferably of Formula (11).

Z is preferably NR^4R^5, especially C_{1-4}-hydroxyalkylamino such as hydroxyethylamino, or OH.

The value of q is preferably greater than or equal to the value of t and (t+q) is preferably 4.

The identity of the divalent organic linking group L is not critical but is preferably C_{2-6}-alkylene, such as eth-1,2-ylene, or optionally substituted phenylene.

G is preferably substituted alkyl, especially C_{1-4}-substituted alkyl; substituted aralkyl, especially substituted phenyl-(C_{1-3}-alkyl); substituted phenyl; or substituted naphthyl wherein at least one of the substituents is selected from -COOH, $-(CH_2)_n$-COOH, $-O-(CH_2)_n$-COOH, $-S-(CH_2)_n$-COOH and $-NR^8(CH_2)_n$-COOH in which n is an integer from 1 to 6 and R^8 is H or C_{1-4}-alkyl. The group G is preferably carboxyphenyl or dicarboxyphenyl.

The cyan dye of Formula (10) is described in greater detail in EP 468,649 the contents of which are incorporated herein by reference.

The present invention relates not only to an ink containing a colorant comprising a black and a yellow and/or a cyan dye as hereinbefore defined in the free acid form, but also in the form of salts, preferably alkali metal, ammonium or substituted ammonium salts, and especially salts derived from ammonia or a volatile amine. Furthermore, although any amino groups in the formulae for the dyes are shown in neutral form, these groups may exist as substituted ammonium cations, especially if the dye is capable of existing in zwitterionic form.

In the salt form, especially as alkali metal, ammonium or substituted ammonium salts or mixtures thereof, at pH 7.5 and above, especially from pH 7.5 to 9.0, the dyes have good solubility in water, often up to 10% or more, by weight. However, the water-solubility drops sharply below pH 7.5 and below pH 6 they are generally insoluble in water and aqueous media.

The cation in the ammonium or substituted ammonium salts is preferably a quaternary ammonium group of the formula $^+NH_pQ_q$ in which

p and q	are each independently integers from 0 to 4 provided that (p+q) = 4, and
each Q	independently is an organic radical; or
2 or 3 Qs,	together with the N atom to which they are attached, form a heterocyclic ring and any remaining Qs are C_{1-4}-alkyl.

Organic radicals represented by Q are preferably C_{1-4}-alkyl, especially methyl; aryl, especially phenyl; or aralkyl, especially benzyl. Heterocyclic rings formed by NQ_4 are preferably 5- or 6-membered heterocycles, such as morpholinyl, piperidinyl or pyridyl.

Examples of quaternary ammonium groups of formula $^{+}NH_pQ_q$ are $^{+}NH_3(CH_3)$, $^{+}NH_2(CH_3)_2$, $^{+}NH(CH_3)_3$, $^{+}N(CH_3)_4$, $^{+}N(CH_2CH_3)_4$, N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethylmorpholinium.

The dyes can be converted into their ammonium or substituted ammonium salts by dissolving in water, as a salt with an alkali metal, acidifying the solution with a mineral acid, adjusting the pH to 9-9.5 with ammonia or an amine or a quaternary ammonium hydroxide and removing alkali metal salt by dialysis.

The inks may be prepared by dissolving the dyes, individually or mixed together to form the colorant, in water alone and optionally adding a water-soluble organic liquid or in an ink medium comprising water and a water-soluble organic liquid. Other ingredients can be added to the ink either before or after the dyes. The ink is preferably filtered prior to use in ink jet printing in order to remove any undissolved matter which can cause blockages in the nozzles of an ink jet printer.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

Examples

Appropriate amounts of the dyes identified in Table 1 were dissolved in the identified ink media in order to prepare the Inks 1 to 11 identified in Table 1 each ink containing 2.5% colorant. The inks were then assessed for printing quality by printing onto an acid paper (Ac, Xerox 4024 DP) and an alkaline paper (Alk, Hammermill Fore DP3V-2) using a Hewlett-Packard Deskjet printer. The parameters measured were print density (PD), luminance (L), colour space coordinates (A & B), wet-fastness (WF (%)), light-fastness (LF (Blue scale rating)) and visual appearance (VA), the latter to detect the presence or absence and extent of bronzing. The components of the ink media (Med) were water (W), 2-pyrrolidone (P) and sulpholane (S) and the proportions (prop) were by weight.

Table 1

Ink	Dye	%	Med & Prop	Paper	PD	L	A	B	WF	LF
2	B1	95	W:P 90:10	Ac	25.5	27.1	2.4	-5.6	97	3
	C1	5		Alk	14.5	34.5	3.8	-7.7	94	3
3	B1	90	W:P 90:10	Ac	23.2	28.4	2.8	-4.9	97	3
	C1	10		Alk	16.5	32.7	3.2	-7.8	94	3
4	B1	95	W:P 90:10	Ac	26.5	26.8	1.7	-3.8	98	3
	Y1	5		Alk	14.7	34.5	2.9	-6.1	92	3
5	B1	90	W:P 90:10	Ac	27.5	26.5	1.1	-3.5	98	3
	Y1	10		Alk	17.8	32.2	2.2	-4.4	91	3
6	B1	95	W:S 95:5	Ac	28.7	25.6	3.5	-4.5	96	3
	C1	5		Alk	18.2	31.3	4.2	-7.3	90	3
7	B1	90	W:S 95:5	Ac	28.9	25.5	3.2	-4.7	96	3
	C1	10		Alk	16.8	32.3	3.9	-8.3	91	3
8	B1	95	W:S 95:5	Ac	27.9	26.1	2.7	-4.0	99	3
	Y1	5		Alk	22.0	29.1	4.0	-4.8	84	3
9	B1	90	W:S 95:5	Ac	28.6	26.0	2.5	-3.0	98	3
	Y1	10		Alk	20.0	30.5	3.1	-4.5	84	3
10	B1	90								
	Y1	5	W:P 90:10	Ac	27.3	26.4	1.5	-4.3	97.5	3
	C1	5								
11	B1	85	W:P 90:10	Ac	26.7	27.0	0.6	-2.8	97.5	3
	Y1	15								

Notes:

Med & Prop is ink medium and proportions by weight

W is water

S is sulpholane

Tr Br is trace bronzing

No Br is no bronzing

Claims

1. An ink comprising a solution of a colorant in an aqueous medium, the colorant comprising at least 80% by weight of a water-soluble black dye of Formula (1) as herebefore defined and up to 20% of one or both of two other water-soluble dyes, one of which is a yellow dye of the Formula (2) as hereinbefore defined and the other is a cyan dye of Formula (9) as hereinbefore defined.

2. An ink according to Claim 1 wherein the colorant comprises from 90% to 98% of the black dye and from 10% to 2% of the yellow dye.

3. An ink according to Claim 1 wherein the colorant comprises from 90% to 95% of the black dye and from 10% to 5% of the cyan dye.

4. An ink according to any one of Claims 1 to 3 wherein the black dye is the dye of Formula (1) wherein W is 3-COOH, X is 5-COOH and Y, Z and R are H, in the ammonium salt form.

5. An ink according to Claim 1 or Claim 2 wherein the yellow dye of Formula (2) in which Ar and Ar^1 are both 3,5-dicarboxyphenyl; J and J^1 are both phen-1,4-ylene; R^1 and R^4 are both H; and n is 0, in the ammonium salt form.

6. An ink according to Claim 1 or Claim 3 wherein the cyan dye is of Formula (9) wherein Pc is copper phthalocyanine; R^1 and R^2 are both H, t is 1 and q is 3, and the COOH group is in the 3-position, in the ammonium salt form.

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Examiner's report to the Comptroller under Section 17
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Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: CA, WPI, CLAIMS

Documents considered relevant following a search in respect of Claims :-
ALL

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Category	Identity of document and relevant passages		Relevant to claim(s)
A	EP 0559309 A2	(ZENECA)*	ALL
A	EP 0565286 A1	(ICI)*	ALL
A	EP 0534634 A1	(HEWLETT-PACKARD)*	ALL
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